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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C11D 3/39</b>		<b>A1</b>	(11) International Publication Number: <b>WO 95/33816</b> (43) International Publication Date: 14 December 1995 (14.12.95)																				
(21) International Application Number: <b>PCT/EP95/01943</b> (22) International Filing Date: <b>22 May 1995 (22.05.95)</b> (30) Priority Data: <b>9411495.6</b> <b>8 June 1994 (08.06.94)</b> <b>GB</b> (71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG only): <b>UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).</b> (71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD SG SZ TT UG): <b>UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</b> (72) Inventors: <b>ALLAN, Alexander; 104 Dibbins Hey, Spital, Bebington, Merseyside L63 9HE (GB). OAKES, John; Farm Bungalow, Darnhall School Lane, Winsford, Cheshire CW7 1LH (GB).</b> (74) Agent: <b>ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).</b>		(81) Designated States: <b>AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</b>  <b>Published</b> <i>With international search report.</i>																					
(54) Title: <b>AQUEOUS BLEACHING COMPOSITIONS COMPRISING PEROXY CARBOXYLIC ACIDS</b>																							
<div style="display: flex; justify-content: space-between;"><div><b>% PEROXYACID REMAINING</b></div><div><b>% DEQUEST 2010 ADDED</b></div></div> <table border="1"><caption>Approximate data from the 3D bar chart</caption><thead><tr><th>% Versenex Added</th><th>0.14% Dequest 2010</th><th>0.28% Dequest 2010</th><th>0.42% Dequest 2010</th></tr></thead><tbody><tr><td>0.000%</td><td>~10</td><td>~30</td><td>~50</td></tr><tr><td>0.013%</td><td>~100</td><td>~110</td><td>~120</td></tr><tr><td>0.040%</td><td>~100</td><td>~110</td><td>~120</td></tr><tr><td>0.070%</td><td>~100</td><td>~110</td><td>~120</td></tr></tbody></table> <div style="text-align: center;"><b>% VERSENEX ADDED</b></div>				% Versenex Added	0.14% Dequest 2010	0.28% Dequest 2010	0.42% Dequest 2010	0.000%	~10	~30	~50	0.013%	~100	~110	~120	0.040%	~100	~110	~120	0.070%	~100	~110	~120
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0.070%	~100	~110	~120																				
(57) Abstract <p>Stability of compositions comprising relatively low levels (0.5-15 wt.%) of peroxycarboxylic acids, particularly PAP, can be improved by formulation such that one or more complexing agents for vanadium, manganese and cobalt are present. A mixture of 1-hydroxy ethylidene (1,1, diphosphonic acid) and diethylene triamine pentacetic acid has been found to be particularly effective.</p>																							

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AQUEOUS BLEACHING COMPOSITIONS  
COMPRISING PEROXY CARBOXYLIC ACIDS

5

Technical Field

10

The present invention relates to improvements in bleaching and/or hygiene compositions comprising organic peroxyacids.

15

While the invention will be described with particular reference to bleaching and/or hygiene compositions for use on hard surfaces such as ceramics, plastics and metals, or in aqueous solutions contacting solid surfaces, it is not intended to be restricted to such compositions and extends to compositions for use in fabrics washing, personal care and other applications where organic peroxyacids are employed.

20

In this specification the terms bleaching agent and hygiene agent are used interchangeably unless otherwise indicated.

25

Background to the Invention

30

For many years it has been known to employ hydrogen peroxide as a water soluble bleaching and hygiene agent. To a lesser extent, other peroxides such as sodium peroxide have been employed as bleaching agents, as have soluble peracids, such as peracetic acid, either as such or as precursors such as tetra acetyl ethylene diamine, as well as performic acid and potassium mono persulphate.

35

Aqueous-insoluble or partially insoluble peroxyacids have also been investigated with particular reference to their use in fabric bleaching compositions and in machine

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dishwashing applications, both in liquid and powder compositions. These have included both organic and inorganic peroxyacids.

5 EP 0435379 (AKZO, 1989) relates to the use of imidoperoxy-carboxylic acids (as defined therein) in bleaching compositions in soaking detergents and dishwashing detergents. Preferred compositions include e-N-N-phthaloyl-amino-peroxy-caproic acid (PAP).

10

The above-mentioned specification discloses that sequestering agents should be present to advantageously bind stray metal ions which might otherwise accelerate the decomposition of the peroxyacid. Suggested sequestering  
15 agents include ethylene diamine tetra-acetate (EDTA), sodium pyrophosphate, phosphoric acid, dipicolinic acid, and organic phosphorous compounds like 1-hydroxy ethylidene (1,1, diphosphonic acid) ('DEQUEST 2010' [RTM]) and amino tri(methane phosphonic acid) ('DEQUEST 2000' [RTM]). These  
20 agents are employed in amounts of 0.01 to 1% by weight of the suspension.

EP 0442549 (UNILEVER, 1990) discloses PAP-containing compositions which are prepared with surfactants containing  
25 low levels of iron and copper as impurities. The proposed sequestering agents include the above-mentioned sequestering agents and two further sequestering agents ethylene diamine tetra-(methylene phosphonic acid) ('DEQUEST 2040' [RTM]) and diethylene triamine penta-  
30 (methylene phosphonic acid) ('DEQUEST 2060' [RTM]).

Other sequestering agents and stabilizers are known, these include disodium hydrogen phosphate, disodium dihydrogen pyrophosphate, sodium tripolyphosphate, sodium stannate,  
35 and methylene diphosphonate.

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Despite the introduction of the above-mentioned sequestering agents compositions containing organic peroxyacids have not proved particularly stable when manufactured on industrial scales. In the presence of 0.14%wt 1-hydroxy ethylidene (1,1, diphosphonic acid) over 90% decomposition of the peroxyacid may occur over storage periods as short as seven days at 37 Celcius. Other sequesterants at equimolar concentrations show little or no improvement. Some sequesterants, such as diethylene triamine pentacetic acid, show very poor stabilizing effects at equimolar concentration (0.34%).

Trace metal analysis of unstable samples prepared on industrial plant as compared with stable samples prepared in laboratory glassware has failed to reveal an excess of any metal in the unstable samples as opposed the stable samples.

#### Brief Description of the Invention

We have now determined that the stability of compositions comprising organic peroxyacids can be improved by selection of specific sequestering agents. Conveniently, these can be described with reference to the particular metals which they sequester.

According to a first aspect of the present invention there is provided an aqueous bleaching composition comprising 0.1-15%wt of an organic peroxyacid which further comprises one or more sequestering agents for each of vanadium, cobalt and manganese.

It is believed that 1-hydroxy ethylidene (1,1, diphosphonic acid), available in the marketplace as 'DEQUEST 2010' is an effective sequesting agent for manganese. However, this

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particular sequestering agent is believed not to sequester vanadium and cobalt. Without wishing to limit the invention by reference to any theory of operation it is currently believed that manganese, vanadium and/or cobalt are introduced into the product during contact with metal vessels, pipes and or fittings and that very low levels of these metals can significantly reduce the stability of the composition.

According to a further aspect of the present invention there is provided a process for the preparation of an aqueous bleaching composition comprising 0.1-15%wt of an organic peroxyacid, a suspending surfactant system and one or more sequestering agents for each of vanadium, cobalt and manganese, CHARACTERISED IN THAT it comprises the steps of

a) preparing a surfactant solution at a temperature in excess of 35 Celcius, and,

b) following step (a) cooling the product of step (a) to less than 30 Celcius and subsequently mixing at least one sequestering agent.

#### Detailed Description of the Invention

As mentioned above, the present invention relates a bleaching composition comprising 0.1-15%wt of an organic peroxyacid which further comprises one or more sequestering agents for each of vanadium, cobalt and manganese.

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Sequestering Agent

5 A characteristic feature of compositions according to the present invention is the presence of the sequestering agent.

10 Preferred metal ion complexing agents are selected from dipicolinic acid, ethylene diamine tetra acetic acid (EDTA) and its salts, hydroxy-ethylidene diphosphonic acid (Dequest 2010, RTM), ethylene diamine tetra (methylene phosphonic acid) (Dequest 2040, RTM), diethylene triamine penta(methylene phosphonic acid) (Dequest 2060, RTM), amino tri(methylene phosphonic acid) (Dequest 2000, RTM) and diethylene triamine pentacetic acid ('VERSENEX (R) 80' 15 RTM).

20 Particularly preferred compositions according to the present invention comprise a first sequestering agent for cobalt and vanadium and a second sequestering agent for manganese.

25 1-hydroxy ethylidene (1,1, diphosphonic acid) is the preferred sequestering agent for manganese. This material is commercially available as 'DEQUEST 2010'.

Diethylene triamine pentacetic acid is the preferred sequestering agent for vanadium and cobalt. This material is commercially available as 'VERSENEX (R) 80'.

30 It is preferred that the initial level of each metal ion complexing agent should fall into the range 0.005-5%wt. More particularly. The initial level of each metal ion complexing agent should fall in the range 0.01-0.25%wt.

35 It should be noted that a mechanism by which the invention is believed to work is not entirely clear. Experimental



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results are confusing in that a comparison of samples prepared in laboratory glassware and in an industrial pilot plant shows only slightly higher levels of metal in the piloy plant samples: typically 0.7ppm iron in the laboratory samples and 1.0 ppm iron in the plant samples. However, comparison of plant prepared samples exhibiting good and poor storage stability fails to show any significant differences in transition metal levels after examination of the levels of around 35 elements. Moreover, analysis of stable samples containing the above-mentioned sequestering agents, particularly VERSENEX 80, shows that the sequestering agent can be both effective in preventing decomposition of the peroxy acid while being rapidly decomposed by what is believed to be a reaction with the peroxy acid.

#### Peroxyacid

Generally the organic peroxyacid will be a peroxy carboxylic acid, more preferably an imido peroxy-carboxylic acid, most preferably e-N-N-phthaloyl-amino-peroxycaproic acid (PAP).

Other peroxy-carboxylic acids, are known as described above and from a publication entitled "TAED and new peroxycarboxylic acids as highly efficient bleach systems", 80th AOCS Meeting, Cincinnati OH, May 1989 and are incorporated herein by reference.

#### pH

Typically the pH of the composition is such that it is above the  $pK_a$  of the corresponding carboxylic acid and below 6.0.

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Preferably, the pH of the composition is greater than 4.5 and less than 6.0.

5 Particularly, when the peroxy acid is PAP, the preferred pH falls into the range 4.8-6.0, and is most preferably around 5.0-5.5. Without wishing to be bound by theory, it is believed that, at a pH below the  $pK_a$  of the corresponding acid the decomposition product of the peroxy carboxylic acid, i.e. the acid in protonated form, is insoluble and  
10 forms white, needle like crystals, while above a pH of 6.0, excessive decomposition of the acid is believed to occur.

#### Surfactants

15 Typically, the composition further comprises a surfactant component. In typical embodiments of the invention the surfactant exists in part at least in the form of a lamellar phase.

20 In preferred embodiments of the invention the surfactant is a sulphate or sulphonate anionic surfactant.

25 In preferred embodiments of the invention the composition further comprises at least 3% of a sulphate salt other than a transition metal sulphate, and, preferably, 5-10% of one or more surfactant stable in the composition.

30 It will be appreciated that commercially available sulphate and sulphonate surfactants often contain sodium sulphate as an impurity. Typical levels being around 5%  $Na_2SO_4/100\%$  AD.

35 It is preferred that the relative levels of these further components is such that the weight ratio of said surfactant to said sulphate is in the range 0.4-0.8:1, more preferably

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0.6-0.8:1, as surfactant:sulphate (both being expressed as sodium salts).

5 The presence of transition metals in the surfactants or the electrolyte either as sulphate salts or otherwise should be minimised.

10 Most preferably, the weight ratio of surfactant:sulphate is around 0.66:1. Without wishing to restrict the invention by reference to a theory of operation, it is believed that, whilst a lamellar thickening system can be formed with a variety of surfactant and electrolyte ratios and over a range of pH values, the most stable compositions are only formed in a particular pH range and with particular ratios  
15 of surfactant to sulphate.

Preferably, the surfactant system comprises secondary alkane sulphonate.

20 It is particularly preferred that compositions are free of surfactants which contain benzene rings as these have not only been found to be less stable than compositions according to the present invention which comprises secondary alkane sulphonate but these surfactants may also  
25 resent environmental problems.

For conventional products, preferred levels of secondary alkane sulphonate range from 4.0-10%wt with levels around 5.3wt% being most preferred. It will be understood that  
30 proportionally higher levels of surfactant will be required for more concentrated products. Products comprising up to 30% surfactant, including four-fold concentrates on conventional products, are envisaged.

35 Most preferably the secondary alkane sulphonate is a C12-C18 average chain length secondary alkane sulphonate.

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Preferably the surfactant system further comprises a nonionic surfactant.

5 Preferred levels of nonionic surfactant are 1-6%wt of an ethoxylated nonionic surfactant. Preferably the nonionic surfactant has an ethoxylation level of 3-12.

10 The most preferred levels of the ethoxylated nonionic are 1-3%wt on total product. Levels toward the lower limit of the range are employed where the optional fatty acid is present.

15 Preferably the surfactant system further comprises fatty acids.

Suitable fatty acids comprise alkyl chains having an average of 12-18 carbon atoms.

20 It is particularly preferred that the surfactant system comprises a mixture of at least secondary alkane sulphonate and fatty acid.

25 More preferably the surfactant system comprises secondary alkane sulphonate, fatty acid and at least one nonionic surfactant. The most preferred weight ratios between these components are 4:1:1.

30 It is preferable that the weight ratio of the alkali metal sulphate to total surfactant falls in the range 1:0.6-1.25, more preferably 1:0.75-1.25.

35 The molecular weight of a typical secondary alkane sulphonate is around 300, whereas the molecular weight of a typical nonionic surfactant of the 'Synperonic' (RTM) type is around 325. Fatty acids of the types described above have molecular weights around 220. Thus, the preferred

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mole ratios between the surfactants are 3-5:1 for the secondary alkane sulphonate to nonionic and 2-5:1 for the secondary alkane sulphonate to fatty acid.

5 The molecular weight of sodium sulphate is 142.04, i.e. about half that of a typical secondary alkane sulphonate. It is preferable the molar ratio of the sulphate to the secondary alkane sulphonate is such that around 3-5 moles of sulphate are present for each mole of secondary alkane  
10 sulphonate. As the levels of sulphate present in technical grades of secondary alkane sulphonate are very much lower than this it will be appreciated that the mere use of technical grades of secondary alkane sulphonate will not achieve preferred embodiments of the invention and an  
15 addition of further sulphate will be required.

Alternative suspending systems, which do not comprise surfactant as an essential ingredient can be employed.

20

#### Minors

Various inessential components may also be present in the compositions according to the invention. These include  
25 colouring agents, opacifiers, perfumes, and solvents.

In order to facilitate processing, and particularly packing of certain compositions according to the present invention, it is convenient that formulations comprise an initial, low  
30 level of a bleach-sensitive antifoam component which is decomposed during storage of the product. Examples of such materials are known in the art. The presence of such a component is optional but is preferable when high foaming surfactant systems are employed.

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Process Aspects

It is believed that certain metal ion complexing agents, in particular the diethylene triamine pentacetic acid (the  
5 'VERSENEX') metal ion complexing agent react with the peroxyacid to a significant extent at a temperature in excess of 35 Celcius.

It is believed that the diethylene triamine pentacetic acid  
10 forms an N-oxide and other reaction products in a very short time at elevated temperatures in the presence of the peroxyacid.

We have determined that improved products can be produced  
15 by a method in which all steps wherein the product is required to be heated to or held at a temperature above 35 Celcius are carried out in the absence of one or more of the metal ion complexing agents. These agents are preferably added after cooling to a temperature of below 30  
20 Celcius. In the alternative, the metal ion complexing agent can be added before exposure to elevated temperatures but the peroxyacid is not added prior to cooling. Thus, the peroxyacid and the peroxyacid-sensitive metal complexing agent are not mixed until after any process  
25 steps which require temperatures in excess of 40 Celcius have been completed.

In a preferred method according to the present invention,  
the surfactants, electrolytes and non-volatile minors are  
30 mixed and heated to a temperature in excess of 40 Celcius prior to cooling and subsequent addition of at least a portion of the metal ion complexing agent.

In order that the present invention may be further  
35 understood it will be illustrated hereafter by way of example.

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EXAMPLES

Formulations were prepared as shown in Table 1 below. The materials are identified as follows:

- 5 Dequest 2010: RTM (ex. Monsanto) sequesterant: 1-hydroxy ethylidene (1,1, diphosphonic acid):
- VERSENEX(R) 80 RTM (ex DOW) sequesterant: diethylene triamine pentacetic acid:
- 10 PAP: e-N-N-phthaloyl-amino-peroxycaproic acid (ex. Ausimont):
- 15 SAS-30: Hostapur (RTM, ex Hoechst) Secondary alkane sulphonate:
- Synperonic A3: (RTM, ex. ICI) alcohol ethoxylate, nonionic surfactant:
- 20 Prifac 5901: (RTM, ex. Unichema) fatty acid:

Sample formulations were prepared by simple mixing of the components at 45 Celcius. The pH of the formulations was regulated by the addition of 20% w/v NaOH to pH 5.0. The overall composition is shown in table 1 below, wherein composition figures are given assuming 100%wt-active for the components:

25

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Table 1

	Sodium Sulphate	8.0%
	PAP	1.8%
5	SAS-30	6.67%
	Symperonic A3	1.67%
	Prifac 5901	1.67%
	DEQUEST 2010	0.14%

10

All products were stored at 37°C for seven days in the dark and the final concentration of PAP was determined by titration under acidic conditions against thiosulphate/KI at 0°C.

15

In order to illustrate the present invention samples were prepared by varying the metal ion complexing agents as shown in figure 1. To avoid problems of reaction between the metal ion complexing agents and the peroxyacid, further doses of the metal ion complexing agents were added after cooling of the samples from 45 to 37 Celcius.

20

As can be seen from the figure, samples were prepared with 0.0, 0.013, 0.04 and 0.07wt% VERSENEX 80, and with 0.14, 0.28 and 0.42wt% DEQUEST 2010. From figure 1 it can be seen that DEQUEST 2010 alone is a poor stabilizer for the composition as very little PAP remains after seven days storage. Increasing the level of DEQUEST has little effect on the overall stability. However, the addition of VERSENEX 80 at levels well below the equimolar concentration had a major effect on stability.

25

30

It can also be seen from figure 1 that addition of larger quantities of the VERSENEX component has a deleterious effect on the stability of the composition. This is

35



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believed to be due to the reaction between the VERSENEX and the peroxyacid as mentioned above.

Figure 2 shows the effect of addition of metal ion solutions to samples having the composition given in table 1 except that the DEQUEST was absent other than where indicated as being present. Metal ions were added as soluble nitrates or chlorides at 1ppm metal (using atomic absorption standards). From figure 2, it can be seen that samples prepared in the absence of DEQUEST are unstable in the presence of manganese, whereas samples prepared in the absence of VERSENEX are relatively unstable in the presence of vanadium and very unstable in the presence of cobalt. Surprisingly, analysis of trace metals in unstable samples prepared on an industrial scale plant did not reveal significant differences between the levels of these particular metals (Co, V, Mn) as compared with stable samples prepared on the same plant under substantially identical conditions.

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CLAIMS

- 5           1.    An aqueous bleaching composition comprising 0.1-15%wt  
            of an organic peroxyacid which further comprises one  
            or more sequestering agents for each of vanadium,  
            cobalt and manganese.
- 10          2.    Composition according to claim 1 wherein the metal ion  
            complexing agents are selected from polycarboxylic  
            acids, and polyphosphonic acids.
- 15          3.    Composition according to claim 2 wherein the metal ion  
            complexing agents are selected from dipicolinic acid,  
            ethylene diamine tetra acetic acid and its salts,  
            hydroxy-ethylidene diphosphonic acid, ethylene diamine  
            tetra (methylene phosphonic acid), diethylene triamine  
            penta(methylene phosphonic acid), amino tri(methylene  
20              phosphonic acid) and diethylene triamine pentacetic  
            acid.
- 25          4.    Composition according to claim 1 comprising a first  
            sequestering agent for cobalt and vanadium and a  
            second sequestering agent for manganese.
5.    Composition according to claim 1 comprising 1-hydroxy  
            ethylidene (1,1, diphosphonic acid).
- 30          6.    Composition according to claim 1 comprising diethylene  
            triamine pentacetic acid.
- 35          7.    Composition according to claim 1 wherein the level of  
            each metal ion complexing agent falls into the range  
            0.005-5%wt.

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8. Composition according to claim 1 wherein the organic peroxyacid will be a peroxy carboxylic acid.
9. Composition according to claim 8 wherein the organic peroxyacid is an imido peroxy-carboxylic acid.
10. Composition according to claim 1 wherein the pH of the composition is such that it is above the  $pK_a$  of the corresponding carboxylic acid and below 6.0.
11. Composition according to claim 1 which further comprises a surfactant component.
12. Composition according to claim 1 comprising 0.1-15%wt of an organic peroxyacid, 0.005-5%wt 1-hydroxy ethylidene (1,1, diphosphonic acid) and 0.005-5%wt diethylene triamine pentacetic acid .
13. A process for the preparation of an aqueous bleaching composition according to claim 12, CHARACTERISED IN THAT it comprises the steps of
- a) preparing a surfactant solution at a temperature in excess of 35 Celcius, and,
- b) following step (a) cooling the product of step (a) to less than 30 Celcius and subsequently mixing the cooled product with at least one sequestering agent.

Fig.1.

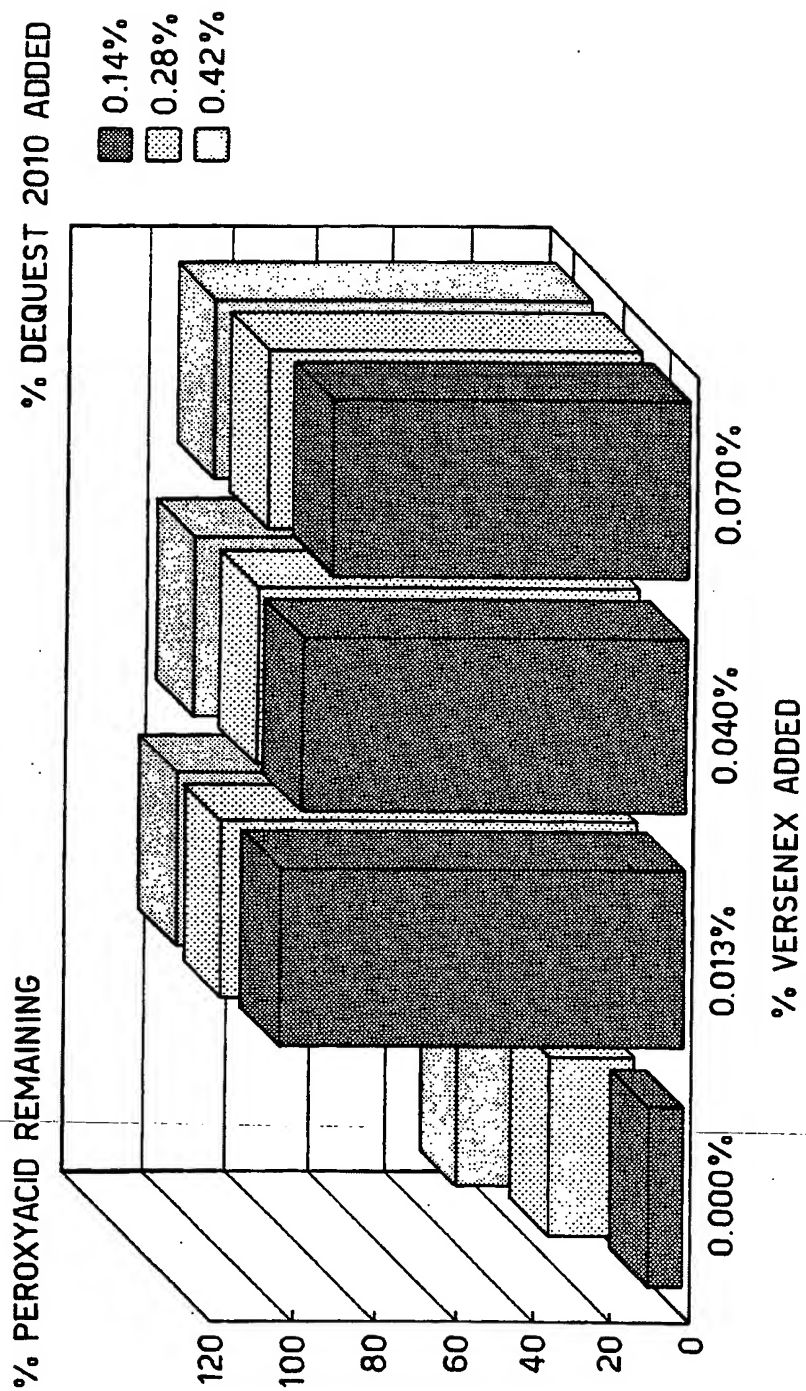
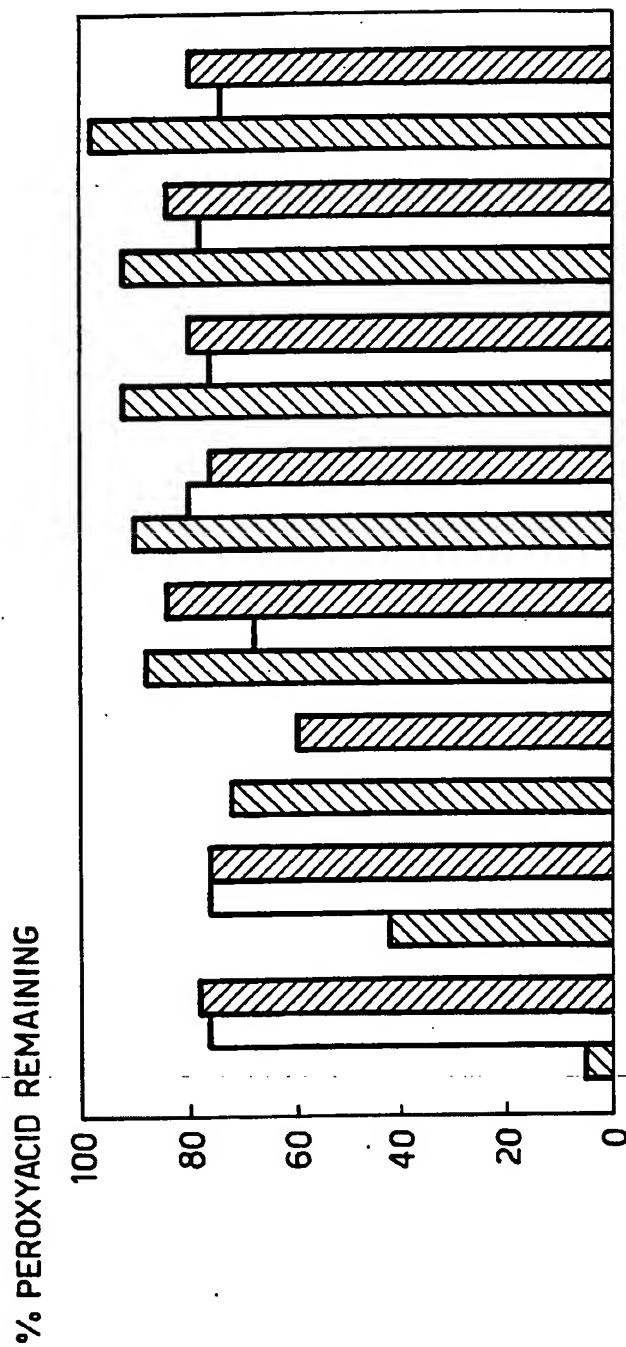


Fig.2.



METAL ADDED	Co	V	Mn	Mo	Ni	Cr	Fe	NONE
D	5	42	72	88	90	92	92	98
V	76	76	8	68	80	76	78	74
D+V	78	76	60	84	76	80	84	80

## INTERNATIONAL SEARCH REPORT

Intern. Classification No  
PCT/EP 95/01943A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/39

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## B. FIELDS SEARCHED

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 515 683 (COLGATE-PALMOLIVE) 6 May 1983 see example 1 ---	1,3
A	WO,A,91 07375 (EKA NOBEL) 30 May 1991 see page 2, line 24 - line 31; claim 1 ---	1-3
A	EP,A,0 384 515 (THE PROCTER & GAMBLE) 29 August 1990 see the whole document ---	1
A	WO,A,93 01716 (ECOLAB) 4 February 1993 see table III ---	1,3
A	EP,A,0 442 549 (UNILEVER) 21 August 1991 see page 6, line 25 - line 29; table 1 -----	1-3,5

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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